THE .... OF DISSOCIATION OF CERTAIN ....

... ORGANIC SALTS IN POTASH AND IN

MIXTURES OF ....

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DISSERTATION

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MARY I. JOHNSON

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ACKNOWLEDGMENT

THE CONDUCTIVITY AND DISSOCIATION OF CERTAIN INORGANIC
AND ORGANIC SALTS IN FORMAMID AND
IN MIXTURES OF FORMAMID WITH
ETHYL ALCOHOL.

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INTRODUCTION.

The conductivity and viscosity study of solutions of elec-
trolytes in formamid was begun in this laboratory by Jones, Davis
and Putnam in 1914.[1]

A resume' of the literature referring to the previous work
on formamid is accessible in the publications referred to above;
therefore it is not desirable to repeat it here.

It was decided to investigate the behavior of a series of
hydrated and non-hydrated salts with common anions--e.g. nitrates--
and with common cations--e.g. sodium salts of typical organic
acids--and finally of a series of formates.

The measurement of the conductivity and viscosity of several
salts in mixtures of formamid and ethyl alcohol, also in formamid
and water mixtures, were contemplated but the many obstacles
offered by the purification of formamid prevented the completion
of more than four salts in the time at our disposal.

APPARATUS

The cells employed for measuring the conductivity of for-
mamid solutions and also those of mixtures consisting of formamid
and alcohol were of the ordinary plate type. The specific con-
ductivities of ethyl alcohol and water used in this investigation
were measured in a cylindrical type of cell. These cells are

(1) Carnegie Inst. Wash. Pub. No. 230, p. 16 (1915):
    Jour. Franklin Inst. Nov. 1915.

described and sketched in a previous publication of Jones. (1)

With the aid of a gas valve and thermo-regulator (2) the temperature baths (3) maintained an average working temperature constant to within 0.01°C. Differential Beckmann thermometers indicated the changes of temperature in each bath. They were adjusted and compared with a standard Reichsanstalt thermometer which had been recently calibrated at the Bureau of Standards in Washington.

Our Leeds-Northup resistance box was also calibrated at the Bureau of Standards.

The improved Kohlrausch slide wire bridge, similar to that used in the earlier work, was used for these measurements.

Jena glass volumetric flasks, calibrated by weight methods, were employed in making up solutions.

A vacuum drying oven (4) devised by Davis and Pardee proved indispensible in preparing the salts for the solutions.

The apparatus for the purification of formamid is described (5) in the previous article.

EXPERIMENTAL PROCEDURE

Purification of Formamid.

From the experience of previous investigators (6) it was learned that formamid was best prepared for conductivity experiments by fractional distillation in an apparatus (7) devised by Davis. The principal difficulties were overcome by maintaining the con-

(1) Carnegie Inst. Wash. Pub. No. 170, p.6 (1912).
(2) Zeit. Physik. Chem. 65, p. 519 (1913).
(3) Carneg. Inst. Wash. Pub. No. 210, p. 21 (1914).
(4) Carneg. Inst. Wash. Pub. No. 210: Pardee Dissertation, p.22.
(5) Carneg. Inst. Wash. Pub. No. 230, p. 16.
(6) Carneg. Inst. Wash. Pub. No. 230, p. 16.
(7) Carneg. Inst. Wash. Pub. No. 230.

ditions of about 2 mm working vacuum with a Gaede pump and a
temperature of 120° - 150° C with a "Crisco" oil bath, during the
fractional distillation process. A very detailed description
of the fractional distillation process, accompanied by photographs
and drawings of the apparatus, is given in the article by the
previous workers.

After formamid had been recovered from salts used in making
fifteen "sets" (1) of solutions, it was found by continued frac-
tionation that a product could be obtained which showed a specific
conductivity of 0.83 X 10^{-5} at 25°. This value is quite comparable
with those obtained when formamid is purified from the commercial
product. The inference drawn from this observation is that the
salts do not alter the purity of the solvent. We also observed
that formamid upon standing in sealed glass-stoppered Erlenmeyer
flasks for a period of four months, June-October, 1916, in a dark
closet increased in specific conductivity only about ten-fold.
The values observed were 0.7 X 10^{-6} and 0.97 X 10^{-5} at 25°.

Formamid with a specific conductivity of 0.70 X 10^{-6} at 25°
offers no great advantage over that with an average specific
conductivity of about 1.5 X 10^{-5} at 25°, with the important excep-
tion of a lower solvent correction.

When formamid was recovered from mixtures with ethyl alcohol
its specific conductivity would reach a value of the order of
1.5 X 10^{-5} at 25° in about the same number of fractionations as
when recovered from pure formamid solutions, but the specific
conductivity soon increased and in the course of three or four
days became too large for conductivity measurements. This

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(1) By "set" is meant all the solvent required for the solutions
    of various dilutions.

suggests a possible reaction between formamid and alcohol, the products of which are more difficult to remove by fractionation than the traces of ammonium formate resulting from hydrolysis of pure formamid by moisture from the air.

Further fractionation, however, yielded a product which maintained a high specific conductivity during the same interval of time as the pure solvent.

If there is a chemical reaction, as suggested above, between alcohol and formamid, the product or products resulting are not known or understood by us. There is another possibility suggested, however which is brought out in the following phenomena: We observed that, when salts were added to the formamid-alcohol mixtures, the concentrated solutions, (N/4 and N/10) did not increase in conductivity by any measurable amount on standing, while the very dilute solution (N/1600) did not increase nearly so rapidly as in the solvent consisting of formamid and alcohol. From this it is quite possible to believe that when formamid and alcohol are mixed there is not only a decrease in association of each but that there is an appreciable dissociation of the alcohol by the formamid. This would account for the increase in conductivity of the mixed solvents over that of either formamid or alcohol, since the mixed solvent containing the greater percentage of formamid has the higher conductivity. This is also substantiated by the viscosity data on these mixtures. This same kind of phenomena is observed in glycerol and water mixtures.

SOLUTIONS

The procedure for making up solutions was the same as that previously employed by Davis and Putnam [1], i.e. by direct weighing for the more concentrated and by diluting the more concentrated.

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(1) Jour. Franklin Inst. Nov. 1915--p. 576.

Great care was used to prevent moisture of the air coming in contact with the solution.

Only 25 cubic centimeters of each solution were prepared as this amount was sufficient both for conductivity and viscosity measurements. All the solutions were prepared at 20°.

Mixed solvents were prepared by weighing a sufficient amount of each solvent for the required percentage mixture. The mixed solvents are made up according to weight normal and not volume normal. All weighings were reduced to a vacuum standard. All other operations in making up solutions of the mixed solvents were similar to those employed in pure formamid.

SALTS.

The salts were prepared for all experiments just before the solutions were made up. The traces of water were removed by a special dehydrating oven [1] at suitable temperatures, and every precaution was used to prevent the salts from absorbing moisture.

We experienced great difficulty in preparing anhydrous calcium nitrate from the pure carbonate. All other salts used in this investigation were prepared pure without great difficulty.

PRECAUTIONS AND ACCURACY.

There are many factors, as hydrolysis, solvation, and polymerization, which enter into the accuracy of the conductivity method to prevent obtaining a true value for the value of $\lambda \infty$. From what has previously been said in connection with the purification of the solvent, it is safe to predict that all three of the factors are producing an effect in case of mixed solvents. Solvation and complexes are believed to be the cause for the increase in molecular conductivity of organic salts and acids of the benzene series.

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[1] Carneg. Wash. Inst. Pub. No. 230--Davis and Pardee.

The molecular conductivity values were repeated for a number of salts, representing each series measured, to within 1/2 mm reading on the bridge for all the concentrated solutions. Therefore, considering the errors in making up "check" solutions, the values below should be approximately correct.

Each "set" (i.e. N/2, N/4, N/10, N/50, etc.) of solutions in pure formamid were made up the day before the conductivity measurements were taken, since experiments showed that measuring the solutions on the same day they were prepared did not increase the accuracy of the work. In the case of mixed solvents, however, it was necessary to make up the solutions and measure them the same day.

Cells were read consecutively in the 15°, 25° and 35° baths. This order was always followed. The bridge readings, however, could be duplicated for the more concentrated solutions when allowed to come to temperature again in the 15° or 25° baths.

EXPLANATION OF TABLES.

In tables I to XXVIII all conductivity values are expressed in reciprocal ohms, and are the molecular conductivities of gram-molecular weights of the various salts. These molecular conductivities (λ_v) were calculated from the equation $\lambda_v = K \dfrac{Va}{Rb}$ where K represents the cell constant, V the volume concentration, R the resistance in ohms as measured by the rheostat, (a) and (b) the readings on the two sides of the bridge. The percentage dissociation α was calculated from the equation $\alpha = \dfrac{100\,\lambda_v}{\lambda_\infty}$ where, λ_∞ is the highest value of λ_v obtained.

The temperature coefficients were derived by means of the formula $\dfrac{(\lambda_v)t_2 - (\lambda_v)t_1}{t_2 - t_1}$ coefficient, in which $(\lambda_v)t_2$ represents at the higher temperature t_2 and $(\lambda_v)t_1$ at the lower temperature t_1. The coefficients expressed as percentages were calculated

from this formula:

$$\frac{(\lambda_V)t_2 - (\lambda_V)t_1}{t_2 - t_1} \times \frac{100}{(\lambda_V)t_1}$$

The values representing the molecular conductivity in these
tables are mean of three bridge readings involving different
values for R.

The term V in the tables represents the number liters
containing a gram molecular weight or are molar solutions;
K expresses the specific conductivity of the solvent.

TABLE I--SODIUM CHLORIDE IN FORMAMID
MOLECULAR CONDUCTIVITY AND DISSOCIATION

V	Molecular conductivity			Dissociation		
	15°	25°	35°	15°	25°	35°
2	10.14	13.22	16.61	50.1	50.1	50.1
4	14.70	19.30	24.61	72.7	73.9	74.0
10	16.76	22.16	28.17	82.9	83.8	84.6
100	19.49	25.46	32.06	96.4	96.3	96.4
200	20.07	26.24	33.02	99.2	99.2	99.3
400	20.21	26.43	33.25	100.0	100.0	100.0
800	20.20	26.36	33.14			
K	.6 X 10^{-5}	.8 X 10^{-5}	1.07 X 10^{-5}			

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent.		Conductivity units	
	15°-25°	25°-35°	15°-25°	25°-35°
2	0.0303	0.0252	0.308	0.339
4	0.0312	0.0275	0.460	0.531
10	0.0322	0.0270	0.540	0.601
100	0.0306	0.0254	0.597	0.660
200	0.0306	0.0257	0.617	0.678
400	0.0306	0.0258	0.622	0.682
800	0.0300	0.0257	0.618	0.676

TABLE II--SODIUM NITRATE IN FORMAMID
MOLECULAR CONDUCTIVITY AND DISSOCIATION

V	Molecular conductivity			Dissociation		
	15°	25°	35°	15°	25°	35°
2	12.96	16.74	21.13	60.8	60.4	61.3
4	15.44	20.23	24.69	72.4	72.9	71.6
10	17.72	23.32	29.72	83.1	84.0	86.2
50	19.38	25.03	31.62	90.9	90.2	91.7
100	20.05	26.18	33.01	94.1	94.4	95.7
200	20.35	26.62	33.20	95.5	95.9	96.3
400	20.77	27.14	33.98	97.5	97.8	98.5
800	21.30	27.73	34.47	100.0	100.0	100.0
1600	21.28	27.56	34.38			
K	.67 X 10^{-5}	.87 X 10^{-5}	1.07 X 10^{-5}			

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent.		Conductivity units	
	15°-25°	25°-35°	15°-25°	25°-35°
2	0.0291	0.0260	0.378	0.439
4	0.0310	0.0220	0.479	0.446
10	0.0317	0.0273	0.560	0.640
50	0.0291	0.0263	0.565	0.659
100	0.0305	0.0260	0.613	0.683
200	0.0306	0.0247	0.627	0.658
400	0.0305	0.0251	0.637	0.684
800	0.0302	0.0243	0.643	0.674
1600	0.0295	0.0247	0.630	0.682

TABLE III --POTASSIUM NITRATE IN FORMAMID

V	Molecular conductivity 15°	25°	35°
2	14.08	18.17	22.72
4	16.67	21.62	26.82
10	19.04	24.39	30.30
50	21.27	27.29	33.90
100	21.90	28.14	34.85
200	22.48	29.05	36.18
400	23.70	30.53	37.84
K	$.945 \times 10^{-5}$	1.24×10^{-5}	1.52×10^{-5}

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent. 15°-25°	25°-35°	Conductivity units 15°-25°	25°-35°
2	0.0290	0.0250	0.409	0.455
4	0.0297	0.0240	0.495	0.520
10	0.0280	0.0242	0.535	0.591
50	0.0283	0.0242	0.602	0.661
100	0.0284	0.0238	0.624	0.671
200	0.0292	0.0245	0.657	0.713
400	0.0288	0.0239	0.683	0.731

TABLE IV--AMMONIUM NITRATE IN FORMAMID

V	Molecular conductivity 15°	25°	35°	Dissociation 15°	25°	35°
2	17.45	22.29	27.50	69.5	69.2	69.3
4	19.39	25.08	31.07	77.3	77.8	78.4
10	22.00	28.00	34.75	87.7	87.0	87.7
50	24.26	30.91	38.48	96.7	96.0	97.1
100	24.34	31.20	38.64	97.0	96.9	97.5
200	24.79	31.76	39.29	98.8	98.6	99.2
400	25.08	32.21	39.59	100.0	100.0	100.0
K	$.94 \times 10^{-5}$	1.24×10^{-5}	1.52×10^{-5}			

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent. 15°-25°	25°-35°	Conductivity units 15°-25°	25°-35°
2	0.0277	0.0233	0.484	0.521
4	0.0293	0.0235	0.569	0.599
10	0.0273	0.0241	0.600	0.675
50	0.0281	0.0244	0.665	0.757
100	0.0286	0.0239	0.686	0.744
200	0.0285	0.0237	0.697	0.753
400	0.0284	0.0235	0.713	0.738

TABLE V-- BARIUM NITRATE IN FORMAMID

V	Molecular conductivity 15°	25°	35°
4	20.90	27.19	34.14
10	28.20	36.93	47.08
50	36.79	47.73	60.77
100	39.73	51.91	65.05
200	40.86	53.16	66.52
400	41.53	53.94	67.39
800	44.20	57.51	71.90
1600	45.24	58.78	74.05
K	$.79 \times 10^{-5}$	$.99 \times 10^{-5}$	1.27×10^{-5}

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent. 15°-25°	25°-35°	Conductivity units 15°-25°	25°-35°
4	0.0300	0.0255	0.829	0.695
10	0.0309	0.0274	0.873	1.015
50	0.0298	0.0273	1.094	1.304
100	0.0306	0.0257	1.218	1.314
200	0.0300	0.0251	1.230	1.336
400	0.0299	0.0249	1.241	1.345
800	0.0300	0.0250	1.331	1.439
1600	0.0296	0.0259	1.354	1.527

TABLE VI--STRONTIUM NITRATE IN FORMAMID

V	Molecular conductivity 15°	25°	35°	Dissociation 15°	25°	35°
4	22.62	30.18	37.62	52.6	53.0	52.7
10	29.46	39.24	49.77	68.6	68.5	69.0
50	37.73	49.73	62.99	87.0	87.0	87.4
100	39.18	51.29	64.82	91.2	90.1	90.7
200	41.09	53.75	67.51	95.6	94.4	94.5
400	42.87	56.75	70.84	99.8	99.7	99.2
800	42.94	56.91	71.38	100.0	100.0	100.0
1600	42.47	55.74	69.30			
K	1.25×10^{-5}	1.32×10^{-5}	1.96×10^{-5}			

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent. 15°-25°	25°-35°	Conductivity units 15°-25°	25°-35°
4	0.0334	0.0246	0.758	0.744
10	0.0326	0.0269	0.958	1.053
50	0.0319	0.0265	1.205	1.326
100	0.0309	0.0263	1.211	1.353
200	0.0308	0.0256	1.266	1.370
400	0.0320	0.0248	1.388	1.409
800	0.0325	0.0254	1.391	1.447

TABLE VII--CALCIUM NITRATE IN FORMAMID

V	Molecular conductivity 15°	25°	35°
10	30.44	39.50	49.37
50	37.80	48.56	60.71
100	41.18	52.98	66.56
200	42.55	54.89	70.13
400	43.46	55.90	72.15
1600	46.03	58.54	75.44
K	1.41×10^{5}	1.91×10^{5}	2.34×10^{5}

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent. $15°-25°$	$25°-35°$	Conductivity units $15°-25°$	$25°-35°$
10	0.0297	0.0249	0.906	0.987
50	0.0284	0.0250	1.076	1.215
100	0.0286	0.0256	1.180	1.358
200	0.0290	0.0274	1.234	1.524
400	0.0286	0.0271	1.244	1.625
1600	0.0272	0.0306	1.251	1.690

TABLE VIII--RUBIDIUM FORMATE IN FORMAMID

V	Molecular conductivity 15°	25°	35°	Dissociation 15°	25°	35°
10	Saturated solution					
50	13.34	16.97	20.90	99.3	98.2	97.1
200	13.44	17.30	21.52	100.0	100.0	100.0
400	12.70	16.41	19.84			
K	$.77 \times 10^{5}$	$.99 \times 10^{5}$	1.24×10^{5}			

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent. $15°-25°$	$25°-35°$	Conductivity units $15°-25°$	$25°-35°$
50	0.0272	0.0231	0.363	0.393
200	0.0287	0.0243	0.386	0.422

TABLE IX--LITHIUM FORMATE IN FORMAMID

V	Molecular conductivity 15°	25°	35°	Dissociation 15°	25°	35°
4	10.42	13.47	16.83	56.5	56.6	57.0
10	13.00	16.82	20.97	70.9	70.9	71.0
50	16.53	21.22	26.49	89.6	89.4	89.8
100	17.24	22.31	27.58	93.4	94.4	93.4
200	17.79	22.90	28.35	96.4	96.3	96.2
400	18.03	23.25	28.88	97.7	98.1	97.8
800	18.26	23.51	29.18	99.0	98.9	98.9
1600	18.44	23.55	29.50	100.0	100.0	100.0
K	.54 X 10⁻⁵	.71 X 10⁻⁵	.87 X 10⁻⁵			

K row: $.54 \times 10^{-5}$, $.71 \times 10^{-5}$, $.87 \times 10^{-5}$

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent. 15°-25°	25°-35°	Conductivity units 15°-25°	25°-35°
4	0.0293	0.0249	0.306	0.335
10	0.0293	0.0246	0.361	0.416
50	0.0283	0.0248	0.438	0.449
100	0.0293	0.0235	0.507	0.525
200	0.0287	0.0238	0.546	0.511
400	0.0289	0.0242	0.454	0.564
800	0.0287	0.0241	0.548	0.567
1600	0.0289	0.0232	0.533	0.572

TABLE X--SODIUM FORMATE IN FORMAMID

V	Molecular conductivity 15°	25°	35°	Dissociation 15°	25°	35°
2	10.32	13.67	17.24	55.8	56.6	56.9
4	12.76	16.48	21.46	68.9	68.2	70.8
10	15.22	19.91	25.00	82.1	82.4	82.5
50	17.35	22.64	28.44	93.8	93.8	93.8
100	18.07	23.61	29.62	97.6	97.7	97.7
200	18.50	24.15	30.29	100.0	100.0	100.0
400	18.45	24.01	30.21			
K	0.8 X 10⁻⁵	1.03 X 10⁻⁵	1.27 X 10⁻⁶			

K row: 0.8×10^{-5}, 1.03×10^{-5}, 1.27×10^{-6}

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent. 15°-25°	25°-35°	Conductivity units 15°-25°	25°-35°
2	0.0324	0.0261	0.335	0.357
4	0.0302	0.0290	0.372	0.498
10	0.0309	0.0256	0.469	0.509
50	0.0305	0.0255	0.529	0.580
100	0.0305	0.0254	0.553	0.601
200	0.0300	0.0254	0.565	0.614

TABLE XI--AMMONIUM FORMATE IN FORMAMID

V	Molecular conductivity			Dissociation		
	15°	25°	35°	15°	25°	35°
10	18.85	24.35	29.99	79.9	90.1	90.9
50	21.86	28.09	34.68	91.2	92.9	93.0
200	23.24	29.82	36.84	97.1	98.7	99.4
400	23.97	30.31	37.04	100.0	100.0	100.0
K	2.01×10^{-5}	2.51×10^{-5}	3.34×10^{-5}			

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent.		Conductivity units	
	15°-25°	25°-35°	15°-25°	25°-35°
10	0.0297	0.0258	0.540	0.577
50	0.0285	0.0234	0.623	0.659
200	0.0281	0.0234	0.653	0.700
400	0.0260	0.0226	0.634	0.693

TABLE XII--STRONTIUM FORMATE IN FORMAMID

V	Molecular conductivity			Dissociation		
	15°	25°	35°	15°	25°	35°
10	Saturated solution					
50	32.40	41.54	51.54	77.9	76.4	79.8
200	37.55	48.71	60.72	89.2	91.1	93.6
400	39.14	51.60	63.74	93.1	94.7	98.2
800	41.37	53.7	65.43	97.1	97.4	98.9
1600	41.52	54.48	67.05	100.0	100.0	100.0
K	$.54 \times 10^{-5}$	$.71 \times 10^{-5}$	$.97 \times 10^{-5}$			

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent.		Conductivity units	
	15°-25°	25°-35°	15°-25°	25°-35°
50	0.0281	0.0251	0.913	1.010
200	0.0298	0.0243	1.116	1.207
400	0.0318	0.0234	1.246	1.214
800	0.0312	0.0232	1.253	1.226
1600	0.0310	0.0231	1.296	1.257

TABLE XIII--BARIUM FORMATE IN FORMAMID

V	Molecular conductivity		
	15°	25°	35°
50	38.35	43.48	53.73
200	37.26	48.97	60.52
400	37.94	49.93	61.69
800	38.59	50.63	62.64
1600	39.27	51.67	63.71
K	.77 X 10^{-5}	.98 X 10^{-5}	1.14 X 10^{-5}

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent.		Conductivity units	
	15°-25°	25°-35°	15°-25°	25°-35°
50	0.0296	0.0235	0.993	1.024
200	0.0311	0.0238	1.161	1.165
400	0.0316	0.0236	1.199	1.176
800	0.0311	0.0236	1.164	1.001
1600	0.0316	0.0233	1.240	1.204

TABLE XIV--SODIUM-BROM-BENZOATE(m) IN FORMAMID

V	Molecular conductivity		
	15°	25°	35°
10	10.47	13.92	17.69
50	14.95	19.50	24.73
K	.8 X 10^{-5}	1.06X10^{-5}	1.32X10^{-5}

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent.		Conductivity units	
	15°-25°	25°-35°	15°-25°	25°-35°
10	0.0330	0.0271	0.345	0.377
50	0.0313	0.0264	0.477	0.527

TABLE XV
SODIUM-NITRO-BENZOATE (m) IN FORMAMID

V	Molecular conductivity 15°	25°	35°
10	10.43	13.95	17.73
50	13.09	17.38	22.08
(200	16.18	21.42	27.12)
(400	21.64	28.50	36.06) ?
(1600	47.08	60.66	74.82,
K	.80 X 10^{-5}	1.06 X 10^{-5}	1.32 X 10^{-5}

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent. 15°-25°	25°-35°	Conductivity units 15°-25°	25°-35°
10	0.0337	0.0269	0.352	0.375
50	0.0323	0.0274	0.433	0.476
(200	0.0323	0.0266)	(0.524	0.570)
(400	0.0320	0.0262)?	(0.694	0.748) ?
(1600	0.0288	0.0233)	(1.358	1.416)

TABLE XVI
SODIUM-AMMO-BENZOATE (m) IN FORMAMID

V	Molecular conductivity 15°	25°	35°
10	10.83	14.34	18.20
50	14.06	18.53	23.34
(200	18.31	23.96	30.23)
(400	23.89	31.17	39.16) ?
(1600	56.24	73.13	91.30)
K	.8 X 10^{-5}	1.06 X 10^{-5}	1.32 X 10^{-5}

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent. 15°-25°	25°-35°	Conductivity units 15°-25°	25°-35°
10	0.0325	0.0269	0.351	0.394
50	0.0318	0.0260	0.447	0.481
200	0.0308	0.0261	0.565	0.627
400	0.0304	0.0256	0.728	0.799
1600	0.0300	0.0254	0.689	0.817

TABLE XVII--SODIUM BENZOATE IN FORMAMID

V	Molecular conductivity			Dissociation		
	15°	25°	35°	15°	25°	35°
4	9.34	12.41	15.73	57.6	60.1	62.1
8	10.94	14.51	18.37	69.2	70.3	72.5
10	11.40	15.03	19.15	71.1	72.8	75.6
50	13.22	17.54	22.25	85.5	85.0	87.8
200	14.32	18.58	23.46	88.7	90.1	92.6
400	14.45	18.81	23.67	90.2	91.1	93.3
1600	16.02	20.62	25.33	100.0	100.0	100.0
K	$0.6X10^{-5}$	$0.8X10^{-5}$	$1.06X10^{-5}$			

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent.		Conductivity units	
	15°-25°	25°-35°	15°-25°	25°-35°
4	0.0353	0.0267	0.317	0.332
8	0.0326	0.0266	0.357	0.386
10	0.0319	0.0273	0.363	0.412
50	0.0326	0.0268	0.432	0.471
200	0.0306	0.0263	0.436	0.488
400	0.0294	0.0259	0.436	0.486
1600	0.0287	0.0223	0.460	0.471

TABLE XVIII--SODIUM SALICYLATE IN FORMAMID

V	Molecular conductivity		
	15°	25°	35°
4	9.65	13.06	16.56
10	11.74	15.51	19.79
50	13.70	18.04	23.95
200	14.49	19.01	24.12
400	14.80	19.27	24.40
1600	17.10	22.13	27.26
K	$0.68X10^{-5}$	$0.83X10^{-5}$	$1.06X10^{-5}$

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent.		Conductivity units	
	15°-25°	25°-35°	15°-25°	25°-35°
4	0.0353	0.0267	0.341	0.350
10	0.0321	0.0276	0.377	0.428
50	0.0317	0.0272	0.434	0.491
200	0.0312	0.0269	0.452	0.511
400	0.0300	0.0266	0.447	0.513
1600	0.0295	0.0232	0.503	0.513

TABLE XIX--SODIUM BENZENE SULPHONATE IN FORMAMID

V	Molecular conductivity 15°	25°	35°
10	12.05	15.87	20.21
50	13.90	18.23	23.06
200	14.52	19.01	24.00
400	14.76	19.04	24.39
1600	16.40	20.90	26.82
K	0.8×10^{-5}	1.06×10^{-5}	1.32×10^{-5}

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent. 15°-25°	25°-35°	Conductivity units 15°-25°	25°-35°
10	0.0317	0.0273	0.382	0.434
50	0.0301	0.0265	0.433	0.483
200	0.0309	0.0262	0.449	0.499
400	0.0290	0.0280	0.428	0.547
1600	0.0274	0.0283	0.450	0.592

TABLE XX--SODIUM SUCCINATE IN FORMAMID

V	Molecular conductivity 15°	25°	35°	Dissociation 15°	25°	35°
10	21.72	28.71	36.59	62.2	64.3	66.6
50	29.54	35.82	49.04	84.4	87.0	89.2
200	32.56	42.67	53.84	90.3	95.6	97.9
400	33.20	43.32	54.24	90.5	97.1	98.6
1600	34.88	44.59	54.95	100.0	100.0	100.0
K	0.6×10^{-5}	0.8×10^{-5}	1.06×10^{-5}			

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

V	Per cent. 15°-25°	25°-35°	Conductivity units 15°-25°	25°-35°
10	0.0321	0.0274	0.699	0.738
50	0.0314	0.0263	0.928	1.012
200	0.0308	0.0252	1.011	1.117
400	0.0304	0.0252	1.012	1.092
1600	0.0298	0.0233	0.979	1.036

TABLE XXI

Tetraethylammonium Iodide:

In 75% Formamid and 25% Ethyl Alcohol

V	Molecular conductivity			Temperature coefficients		Conductivity units	
	15°	25°	35°	15°-25°	25°-35°	15°-25°	25°-35°
4	13.31	17.13	21.14	0.0287	0.0234	0.382	0.401
10	19.96	25.70	31.72	0.0287	0.0234	0.574	0.602
50	23.38	29.76	36.86	0.0274	0.0238	0.638	0.710
100	24.64	31.44	38.91	0.0276	0.0237	0.680	0.747
200	24.75	31.69	39.15	0.0280	0.0236	0.694	0.746
400	24.96	31.95	39.53	0.0280	0.0237	0.699	0.758
1600	24.82	31.95	39.24				
K	1.0×10^{-5}	1.25×10^{-5}	1.57×10^{-5}				

In 50% Formamid and 50% Ethyl Alcohol

V	15°	25°	35°	15°-25°	25°-35°	15°-25°	25°-35°
4	18.80	23.29	28.59	0.0239	0.0227	0.449	0.530
10	22.23	27.92	33.94	0.0250	0.0219	0.559	0.613
50	27.24	34.01	41.30	0.0248	0.0214	0.677	0.729
100	29.49	36.71	44.67	0.0245	0.0216	0.722	0.796
200	29.96	37.24	45.26	0.0245	0.0215	0.734	0.802
400	31.00	38.64	46.95	0.0246	0.0215	0.765	0.831
K	1.01×10^{-5}	1.24×10^{-5}	1.49×10^{-5}				

In 25% Formamid and 75% Ethyl Alcohol

V	15°	25°	35°	15°-25°	25°-35°	15°-25°	25°-35°
4	Saturated solution						
10	22.28	27.86	33.92	0.0219	0.0208	0.482	0.560
50	29.21	35.56	42.61	0.0219	0.0198	0.635	0.705
100	32.43	39.41	47.17	0.0215	0.0194	0.698	0.776
200	34.08	41.34	49.36	0.0213	0.0194	0.726	0.802
400	36.04	43.79	52.29	0.0215	0.0194	0.775	0.850
800	36.72	44.46	53.15	0.0210	0.0195	0.774	0.869
1600	38.13	46.08	54.90	0.0209	0.0191	0.795	0.882
K	1.56×10^{-5}	1.80×10^{-5}	1.99×10^{-5}				

Specific conductivity of Formamid used to prepare
above solvents - 1.41×10^{-5} at 25°
Specific conductivity of ethyl alcohol used to prepare
above solvents - 4.1×10^{-7} at 25°

TABLE XXII

RUBIDIUM IODIDE:

In 75% Formamid and 25% Ethyl Alcohol

V	Molecular conductivity			Temperature coefficients		Conductivity units	
	15°	25°	35°	15°-25°	25°-35°	15°-25°	25°-35°
4	20.00	25.71	31.55	0.0285	0.0227	0.571	0.584
10	22.30	28.45	35.15	0.0275	0.0235	0.615	0.670
50	24.70	31.45	38.75	0.0273	0.0232	0.675	0.730
100	25.69	32.78	40.50	0.0275	0.0235	0.709	0.772
200	25.92	33.04	40.88	0.0275	0.0237	0.712	0.784
400	26.25	33.48	41.50	0.0275	0.0239	0.733	0.803
1600	26.73	34.12	42.27	0.0276	0.0239	0.739	0.815
K	0.75×10^{-5}	0.96×10^{-5}	1.21×10^{-5}				

In 50% Formamid and 50% Ethyl Alcohol

V	15°	25°	35°	15°-25°	25°-35°	15°-25°	25°-35°
4	21.39	26.83	32.60	0.0254	0.0215	0.544	0.577
10	24.59	30.64	37.12	0.0246	0.0211	0.605	0.648
50	28.47	35.41	43.00	0.0244	0.0214	0.694	0.759
100	29.50	36.75	44.58	0.0245	0.0213	0.715	0.783
200	30.25	37.69	45.83	0.0245	0.0216	0.744	0.815
400	30.90	38.47	46.71	0.0244	0.0214	0.757	0.824
1600	32.02	39.77	48.12	0.0242	0.0210	0.775	0.835
K	0.55×10^{-5}	0.70×10^{-5}	0.87×10^{-5}				

In 25% Formamid and 75% Ethyl Alcohol

V	15°	25°	35°	15°-25°	25°-35°	15°-25°	25°-35°
4	20.92	25.27	30.03	0.0208	0.0188	0.436	0.476
10	24.75	29.98	35.61	0.0211	0.0187	0.523	0.563
50	30.49	37.06	44.05	0.0215	0.0188	0.627	0.699
100	32.80	39.85	47.40	0.0215	0.0189	0.705	0.755
200	34.06	41.44	49.38	0.0216	0.0191	0.738	0.793
400	35.13	42.75	51.02	0.0216	0.0193	0.762	0.826
1600	36.69	44.54	53.28	0.0214	0.0194	0.785	0.878
K	$.425 \times 10^{-5}$	$.515 \times 10^{-5}$	$.608 \times 10^{-5}$				

Specific conductivity of formamid used to prepare
above solvents – 1.61×10^{-5} at 25°
Specific conductivity of ethyl alcohol used to prepare
above solvents – 4.1×10^{-7} at 25°

TABLE XXIII

LITHIUM NITRATE:

In 75% Formamid and 25% Ethyl Alcohol

V	Molecular Conductivity			Temperature coefficients		Conductivity units	
	15°	25°	35°	15-25°	25-35°	15-25°	25-35°
10	10.71	23.70	26.12	0.0200	0.0228	0.402	0.542
50	21.45	27.09	33.50	0.0263	0.0239	1.805	0.823
200	22.70	28.83	34.41	0.0303	0.0228	0.807	0.658
400	22.85	29.98	33.81	0.0273	-----	0.583	-----
1000	22.78	29.04					
	K .64x10⁻⁵	1.02x10⁻⁵	1.37x10⁻⁵				

In 50% Formamid and 50% Ethyl Alcohol

10	20.95	24.74	29.02	0.0180	0.0209	0.379	0.518
50	23.72	29.07	33.07	0.0051	0.0214	0.485	0.830
200	25.97	32.00	31.03	0.0215	0.0210	0.032	0.634
400	25.41	32.94	40.56	0.0201	0.0218	0.087	0.772
1000	27.21	33.11	3.71	0.0165	0.0234	0.707	1.024
	K .75x10⁻⁵	.93x10⁻⁵	1.31x10⁻⁵				

In 25% Formamid and 75% Ethyl Alcohol

10	19.21	23.81	26.12	0.0214	0.0181	0.160	0.431
50	25.12	30.85	36.82	0.0210	0.0193	0.536	0.397
200	28.57	34.84	41.53	0.0219	0.0192	0.61	0.069
400	29.64	36.23	43.27	0.0222	0.0194	0.689	1.704
1000	30.63	36.84	0.73	0.0243	0.0217	0.761	0.829
	K .64x10⁻⁷	.7x10⁻⁵	.64x10⁻⁵				

Specific conductivity of formamid used to prepare above solvents - .08 x10⁻⁵ at 25°

Specific conductivity of alcohol used to prepare above solvents - 4.1 x 10⁻⁷ at 25°

TABLE XIV

CALCIUM NITRATE:

In 75% Formamid and 25% Ethyl Alcohol

V	Molecular conductivity			Temperature coefficients		1 mhm J.U.%	
	15°	25°	35°	15-25°	25-35°	1-25°	25-35°
10	61.06	61.61	56.79	0.0571	0.0527	0.839	0.96
50	41.57	31.0	61.3	0.0601	0.0551	1.105	1.281
100	44.79	55.53	75.15	0.1272	0.0521	1.220	1.315
200	46.45	59.07	71.79	0.0878	0.0252	1.204	1.372
400	40.30	51.98	71.33	0.0850	0.0836	1.308	1.504
1600	43.36	51.57	70.05	0.0809	0.0975	1.401	1.063

K 1.80X10⁻⁵ 7.40X10⁻⁵ 3.00X10⁻⁵

In 50% Formamid and 50% Ethyl Alcohol

10	27.58	34.90	41.30	0.0947	0.0905	0.172	0.706
50	41.14	50.97	61.63	0.0208	0.0800	0.983	1.008
100	43.18	53.90	61.00	0.0834	0.0815	1.018	1.139
200	44.54	51.10	74.00	0.0244	0.0208	1.518	1.384
400	50.03	60.14	78.41	0.0251	0.0803	1.311	1.337
1600	54.69	66.81	81.00	0.0065	0.0187	1.342	1.2.7 ?

K 1.80X10⁻⁵ 1.90X10⁻⁵ 2.40X10⁻⁵

In 25% Formamid and 75% Ethyl Alcohol

10	19.48	25.57	27.73	0.0199	0.0185	0.339	0.473
50	33.05	39.21	41.07	0.0192	0.0177	0.518	0.686
100	37.09	43.08	46.78	0.0190	0.0170	0.779	0.770
200	43.17	51.76	66.70	0.0101	0.0172	0.001	0.899
400	48.19	57.93	66.35	0.0600	0.0170	0.974	1.042
1600	55.88	67.86	79.06	0.0205	0.0182	1.148	1.230

K 1.05X10⁻⁵ 1.30X10⁻⁵ 1.54X10⁻⁵

Specific conductivity of pure formamid used to prepare above solvents – 1.08 X 10⁻⁵ at 25°

Specific conductivity of pure alcohol used to prepare above solvents – 4.1 X 10⁻⁷ at 25°

DISCUSSION OF THE RESULTS.

TABLE XXV

Comparison of Conductivity and Dissociation of Nitrates

in Formamid and in Water at 25°C.

Nitrate	Formamid λ_{10}	α	Water(1) λ_8	α
Lithium	21.88	87.0	79.7	79.5
Sodium	23.32	84.0	90.9	77.9
Potassium	24.38	80.0	111.0	79.5
Rubidium	25.59	90.0	118.1	--
Caesium	25.76	87.0	120.0	--
Ammonium	28.00	87.0	113.5	82.0
Barium	36.93	63.0?	146.4	61.1
Strontium	39.24	69.0	154.6	64.6
Calcium	39.50	68.0?	157.3	64.8

From the data arranged in Table XXV several conclusions may
be suggested. First, the values for the molecular conductivity
of nitrates in formamid are much less than in water and also are
of the same order of magnitude in each solvent with the exception
of ammonium nitrate.

Lithium nitrate crystallizes with more water than does
sodium potassium or ammonium nitrate. According to the theory
of Jones and others[2] this means that the lithium ion is more sol-
vated in solutions than are the ions of sodium, potassium or am-
monium. The effect is that lithium ions move more slowly than
those of the other alkali ions, and, consequently the conductiv-
ities are much smaller. The Solvate Theory is a plausible ex-
planation for the smaller conductivity values of lithium ions

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(1) These values were taken from Carnegie Inst. Pub. No. 170.
(2) Carnegie Inst. Pub. No. 170, p. 67.

regardless of their much smaller mass and atomic volume.

The conductivities of the solvated nitrates of barium, strontium and calcium in formamid are analogous in every respect to the conductivity phenomena of these salts in water. As an indication of this the temperature coefficients of conductivity are higher for these salts than for the non-hydrated salts. The alkali salts which have little or no solvating power show approximately the same temperature coefficients of conductivity while those of the alkali earths are higher. We interpret this upon the basis of a decrease in the complexity of the solvate, with rise in temperature.

The relative dissociating power of formamid and water can be shown either by comparing the percentage dissociation of solutions having the same normality or by comparing the solutions when complete dissociation is reached. Table No. XXV has been arranged according to this plan and confirms the strong dissociating power of formamid. It is to be noted that the degree of dissociation of nitrates in formamid is greater than in water, which supports the Thomson-Nernst view, that the dielectric constant is an index to the dissociating power of liquids.

The molecular conductivity of nitrates at infinite dilution was reached in all except barium and calcium nitrate at a dilution not exceeding N/1600. It was considered advisable not to measure solutions of greater dilution than N/1600 because at this dilution the solvent correction for many of the series of salts reached a value equal to or greater than one-half of the total value for the observed conductivity.

In general, the phenomena we are interpreting thru conductivity values show for both hydrated and non-hydrated salts in

formamid analogous behavior to that shown in water.

TABLE XXVI

Comparison of Conductivity and Dissociation of Formates

in Formamid and in Water at 25°C.
(1)

| Formate | Formamid | | Water | |
	Λ_{50}	α	Λ_{32}	α
Rubidium	15.97	98.0	--	--
Lithium	21.22	89.4	--	--
Sodium	22.64	93.8	13.02	87.9
Ammonium	28.09	92.9	--	--
Strontium	41.54	76.0?	--	--
Barium	43.48	84.0?	160.60	76.5

It is to be observed from the data for formates that their percentage dissociation is about the same as those of the nitrates at comparable dilutions but the conductivity values are much less. This is the same effect as in aqueous solutions. The behavior of conductivity in formates is in general the same as that of inorganic salts in formamid.

TABLE XXVII

Comparison of Conductivity and Dissociation of Sodium

Salts of Organic Acids in Formamid and in

Water at 25° . (2)

| Sodium Salt | Formamid | | Water | |
	Λ_{50}	α	Λ_{32}	α
m-Brombenzoic Acid	13.92	--	67.2	--
m-Nitrobenzoic Acid	13.95	--	--	--
m-Aminobenzoic Acid	14.34	--	65.9	--
Benzoic Acid	15.03	--	68.7	--
Salicylic Acid	15.51	--	68.3	--
Benzene Sulphonic Acid	15.87	76.0	69.1	--
Succinic Acid	28.71	--	81.7	--

(1) Results taken from Carneg. Wash. Pub. No. 170 and No. 230.
(2) Results taken from Scudder's tables of conductivities.

This table brings out very clearly that the conductance capacity of the first three salts and also of the next three are of the same magnitude.

All of the mono-basic acid salts have very nearly the same conductance, while the di-basic salt, being a ternary electrolyte, has about twice their conductance. This same fact is brought out by the recent work of Loyd and Pardee [1] in their data for conductivity in pure alcohol.

The conductivity of the first three salts in the table showed a remarkable increase in dilute solutions. The sodium salts of these organic acids tend to increase in conductivity upon standing.

Apparently no relation is brought out by the conductivity values in regard to the constitution of the organic salts.

We attempted to measure the conductivity of benzoic and salicylic acids in formamid with the result that the conductivity value increased about one integer an hour. Therefore we abandoned them. Walden [2], however, has measured the conductivity of some aliphatic acids and does not mention this phenomena.

(1) Carnegie Inst. Wash. Pub. No.   (1917).

(2) Bull. Imp. Acad. Sci. St. Petersburg (1911). Translation
        in German.

TABLE XXVIII

Comparison of Molecular Conductivity in Mixtures
of Formamid and Ethyl Alcohol at 25°.

Tetraethylammonium Iodide

V	HCONH$_2$ 100%	75%	50%	25%	C$_2$H$_5$OH 100%
10	20.51	25.70	27.92	27.86	Insoluble
50	22.69	29.76	34.01	35.56	"
100	23.79	31.44	36.71	39.41	"
200	24.28	31.69	37.24	41.54	"
400	---	31.95	38.64	43.79	"
1600	---	31.95	---	46.08	"

Rubidium Iodide

10	24.00	28.45	30.64	29.98	Insoluble
50	25.27	31.45	35.41	37.06	"
100	26.06	32.78	36.75	39.85	"
200	26.41	33.04	37.69	41.44	"
400	---	33.48	38.47	42.73	"
1600	---	34.12	39.77	44.54	"

Lithium Nitrate

10	20.58	23.70	24.74	23.81	18.25 (1)
50	22.29	27.07	29.57	30.85	26.47
200	23.66	28.83	32.09	34.84	32.31
400	23.63	29.08	33.04	36.23	34.12
1600	---	29.04	35.11	38.24	37.63

Calcium Nitrate

10	39.50	39.41	34.30	23.37	8.36 (2)
50	48.56	52.82	50.97	38.21	15.83
100	52.98	56.99	53.30	45.08	19.56
200	54.89	59.07	61.66	51.78	23.81
400	55.90	61.92	65.14	57.93	25.19
1600	58.54	61.57	68.51	67.36	35.40

One of the most important facts brought out in Table XXVIII is that the so-called normal electrolyte-tetraethylammonium iodide, rubidium iodide and lithium nitrate show an increase in molecular

(1) Carnegie Inst. Wash. Pub. No. 80, p. 84.
(2) Carnegie Inst. Wash. Pub. No. 80, p. 97.

conductivity up to a concentration of 25% formamid and 75% ethyl alcohol mixture. Lithium nitrate was the only salt of these three whose conductivity values in ethyl alcohol were available and their values are about of the same order of magnitude as those in pure formamid, or show that a __maximum is reached__ in conductivity.

This relation interpreted in terms of previous work on other[1] solvents means that there is an increase either in the mobility of the ions or in the dissociation in mixtures with 75% ethyl alcohol and 25% formamid, or both.

The conductivity values for mixtures containing calcium nitrate give evidence of greater variation than the other salts in analogous mixtures. It is seen in Table XXVIII that the maximum in the values for molecular conductivity does not occur in 25% formamid and 75% ethyl alcohol mixtures as for the other salts, but the maxima appear in the concentrated formamid mixture and in the concentrated solutions. The conductivity is greater in the 75% - 25% mixture than in the formamid itself.

From these few salts it is not perhaps justifiable to form any generalization in regard to the conductivity of mixtures.

(1) Carnegie Inst. Wash. Pub. No. 80, p. 58.

SUMMARY OF CONCLUSIONS.

1. Formamid is more difficult to recover from alcohol-formamid mixtures and solutions than from pure formamid for conductivity purposes.

2. Dissociation of inorganic and organic salt solutions is more complete in this solvent than in any previously studied.

3. Typical mono-basic sodium salts of the benzene series have smaller percentage temperature coefficients of conductivity than the di-basic one. The conductivity of these salts constantly increases in dilute solutions.

4. Mixtures of formamid and ethyl alcohol solutions of tetraethylammonium iodide, rubidium iodide, lithium nitrate and calcium nitrate give decided maximum values for conductivity in certain percentage mixtures. The greater the percentage of alcohol in the mixtures, the greater are the conductivity values. This is the opposite of the effect produced in water and alcohol mixtures.

BIOGRAPHY

The author of this dissertation was born in Hagerstown, Maryland, January 28, 1889. After graduating from the Washington County High School in 1909, he finished the courses required for the A.B. and A.M. degrees at Roanoke College, Salem, Virginia in 1912. During the school sessions of 1912-14 he was Instructor of Natural Sciences at Daleville College, Daleville, Virginia. In the Fall of 1914 he entered Johns Hopkins University as a graduate student in Chemistry. Physical Chemistry and Mineralogy were his subordinate subjects. He received University scholarships for the years 1914 and 1916.